

AMENDMENTS TO THE SPECIFICATION

Please replace the paragraph on page 3, line 21 to page 5, line 14 with the following amended paragraph:

PCT International Publication Number WO 2004/60846 discloses a process for producing acetic acid in which acetic acid is produced at a production rate (STY) of 15 mol/L·hr or more at a water content of 2 percent by weight or less and a rhodium content of 1000 ppm or more. According to this document, a reaction for producing methane ($\text{CH}_3\text{OH} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) takes priority over ~~an aqueous~~ a water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$), and water forms and accumulates in the reaction system at a water content in the reaction system of 5 percent by weight or less. To avoid this, the method uses methyl acetate in the reaction system for chemically controlling the water content. The added methyl acetate comes in contact with water in the system and is hydrolyzed into acetic acid and methanol. The resulting methanol is used as a raw material for the production of acetic acid. The increased rhodium content in the system, however, increases not only the production rate of acetic acid but also that of by-produced acetaldehyde. Acetic acid and acetaldehyde increase proportionally with increase in rhodium content. Specifically, acetaldehyde increases substantially proportionally with increase in acetic acid. At a low water content, the rate of aqueous gas shift reaction decreases to thereby decrease the hydrogen partial pressure. At such a low hydrogen partial pressure, the rates of hydrogenation reactions of acetaldehyde (e.g., $\text{CH}_3\text{CHO} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH}$) decrease to thereby increase the acetaldehyde content of the reaction mixture and increase the rate of condensation reactions of acetaldehyde. Consequently, reducing substances such as crotonaldehyde and 2-ethylcrotonaldehyde as products consecutive reactions of acetaldehyde increase to thereby cause poor results in a potassium permanganate test of the product acetic acid. The present inventors have verified the above facts as a result of investigations. In contrast, at a somewhat high hydrogen partial pressure, e.g., at a hydrogen partial pressure of 11 to 14 psi (75.8 to 96.5 kPa) as described in PCT International Publication Number WO 2004/60846, water formed upon by-production of methane must be removed. This requires extra energy and an extra agent for removing water and thereby reduces the production efficiency.

This also increases the by-production of formic acid that is a reducing substance and causes poor results in a potassium permanganate test.

Please replace the paragraph on page 20, line 16 to page 21, line 15 with the following amended paragraph:

The water content of the reaction mixture is generally about 15 percent by weight or less (for example, about 0.1 to about 15 percent by weight), preferably about 10 percent by weight or less (for example, about 0.3 to about 10 percent by weight), more preferably about 5 percent by weight or less (for example, about 0.5 to about 5 percent by weight), and particularly preferably about 3 percent by weight or less (for example, about 0.7 to about 3 percent by weight). An excessively high water content may increase the energy load for separating water in a purification system and requires large purification facilities. At low water contents under conventional reaction conditions, the rate of ~~an aqueous~~ a water gas shift reaction decreases, the hydrogen partial pressure decreases, and by-production of condensation reaction products of acetaldehyde increases to thereby impair the quality of acetic acid. According to the present invention, however, the quality of acetic acid can be satisfactorily maintained without reducing the productivity thereof by carrying out the reaction at a CO partial pressure of 1.05 MPa or more and/or at a methyl acetate content of the reaction mixture of 2 percent by weight or less; keeping the production rate of acetaldehyde to 1/1500 or less the production rate of acetic acid; and maintaining the acetaldehyde content of the reaction mixture to 500 ppm or less.

Please replace the paragraph beginning page 23, line 6 with the following amended paragraph:

The hydrogen partial pressure in the gaseous phase of the reactor is generally about 200 kPa or less, preferably about 100 kPa or less, and more preferably about 70 kPa or less. A high hydrogen partial pressure accelerates a methane-producing reaction ($\text{CH}_3\text{OH} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$), an acetaldehyde-producing reaction ($\text{CH}_3\text{OH} + \text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$), and a

propionic acid-producing reaction ($\text{CH}_3\text{CHO} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{OH} + \text{HI} \rightarrow \text{CH}_3\text{CH}_2\text{I} + \text{H}_2\text{O}$, $\text{CH}_3\text{CH}_2\text{I} + \text{CO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{HI}$). These reactions can be inhibited by reducing the hydrogen partial pressure. Hydrogen is mainly formed by ~~an aqueous~~ a water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$). The hydrogen partial pressure can therefore be reduced by reducing the water content of the reaction mixture. As is described above, at a reduced hydrogen partial pressure under conventional reaction conditions, by-production of condensation reaction products of acetaldehyde increases to thereby impair the quality of product acetic acid. According to the present invention, however, the quality of acetic acid can be satisfactorily maintained without reducing the productivity thereof even at a low hydrogen partial pressure, by carrying out the reaction at a CO partial pressure of 1.05 MPa or more and/or at a methyl acetate content of the reaction mixture of 2 percent by weight or less; keeping the production rate of acetaldehyde to 1/1500 or less the production rate of acetic acid; and holding the acetaldehyde content of the reaction mixture to 500 ppm or less. The lower limit of the hydrogen partial pressure is, for example, about 5 kPa and generally about 10 kPa. The hydrogen is formed as a result of the aqueous gas shift reaction and, additionally, may be introduced into the system together with raw material carbon monoxide.

Please replace the paragraph on page 28, line 2 to page 30, line 10 with the following amended paragraph:

Fig. 1 is a production flow chart showing an embodiment of the production method according to the present invention. In this embodiment, carbon monoxide 1, ~~fresh-methanol-2~~ methanol 2, and, according to necessity, water are continuously fed to a carbonylation reactor 3. The liquid content in the reactor 3 is automatically kept to a predetermined level. The carbon monoxide 1 is preferably introduced to just below a stirrer equipped in the reactor 3. A gaseous purging flow 4 is exhausted from the reactor 3 to thereby prevent the accumulation of gaseous byproducts and maintain a set carbon monoxide partial pressure at a constant total pressure of the reactor. The reactor temperature is automatically controlled. A liquid product (reaction mixture) 5 is extracted from the reactor 3 at such a sufficient rate as to maintain the constant liquid level, introduced into the middle portion between the top and the bottom of an evaporator (flasher) 6,

and subjected to evaporation [Step (A)]. In the evaporator 6, a catalyst mixture is extracted as a bottom flow 7 and returned to the reactor 3 [Step (C)]. The bottom flow 7 mainly comprises acetic acid containing the rhodium catalyst and the iodide salt together with small amounts of methyl acetate, methyl iodide, and water. An overhead 8 of the evaporator 6 mainly comprises product acetic acid and further comprises methyl iodide, methyl acetate, and water. The overhead 8 is introduced to the bottom, the vicinity of the bottom, or the side of a low-boiling component-acetic acid separation/distillation column (low-boiling component-acetic acid splitter column) 9 and subjected to distillation [Step (B)]. A distillate (overhead) 10 of the low-boiling component-acetic acid separation/distillation column 9 mainly comprises methyl iodide and methyl acetate with small amounts of water and acetic acid. The distillate 10 is subjected to a step 11 for removing carbonyl impurities [Step (D)] and returned via a line (reactor recycling line) 12 to the reactor 3 [Step (E)]. A high-boiling component 13 is extracted from the side in the vicinity of the bottom (or from the bottom) of the low-boiling component-acetic acid separation/distillation column 9 and is introduced into an acetic acid-distillation column 14 at the side thereof and subjected to distillation. Then, crude acetic acid 15 is extracted from the bottom or from the side in the vicinity of the bottom of the acetic acid-distillation column 14 [Step (F)]. A low-boiling component 16 including water is discharged out from the top of the acetic acid-distillation column 14, and high-boiling components 17 having a boiling point higher than that of acetic acid are discharged out from the bottom thereof. The low-boiling component 16 is recycled to the reactor 3. It is also possible to arrange a distillation column for distilling off water before the acetic acid-distillation column 14 and to feed the bottom flow of this column to the acetic acid-distillation column 14. The crude acetic acid 15 is further fed to a treatment tank 18 ~~filled~~ packed with a silver- or mercury-exchanged cation exchange resin [Step (G)]. In this step, alkyl iodides, such as hexyl iodide, contained in acetic acid in trace amounts are efficiently separated and removed to thereby yield high-quality acetic acid (product) 19.

Please replace the paragraph on page 31, line 22 to page 33, line 5 with the following amended paragraph:

Fig. 2 is a production flow chart showing another embodiment of the production method according to the present invention. In this embodiment, a liquid product (reaction mixture) 5 from a reactor 3 is introduced to the side of a distillation column 9' and subjected to distillation [Step (A) and Step (B)]. A distillate (overhead) 10' of the distillation column 9' mainly comprises methyl iodide, methyl acetate, and water with a small amount of acetic acid, is subjected to a carbonyl impurities removing step 11 [Step (D)] and returned via a line 12 to the reactor 3 [Step (E)]. The carbonyl impurities removing step 11 is conducted in the same manner as in Fig. 1. A catalyst mixture mainly comprising acetic acid containing rhodium catalyst and the iodide salt with small amounts of methyl acetate, methyl iodide, and water is extracted as a bottom flow 7 from the bottom of the distillation column 9' and is returned to the reactor 3 [Step (C)]. A high-boiling component 13' extracted from the side of the distillation column 9' is introduced into an acetic acid-distillation column 14 at the side thereof and is subjected to distillation. A crude acetic acid 15 is extracted from the side in the vicinity of the bottom of the acetic acid-distillation column 14 [Step (F)]. Water and other low-boiling components 16 are discharged out from the top of the acetic acid-distillation column 14, and high-boiling components 17 having a boiling point higher than that of acetic acid are discharged out from the bottom thereof. The low-boiling components 16 are recycled to the reactor 3. The crude acetic acid 15 is further fed to a treatment tank 18 ~~filled~~ packed with a silver- or mercury-exchanged cation exchange resin [Step (G)]. Thus, alkyl iodides such as hexyl iodide contained in acetic acid in trace amounts are efficiently separated and removed to thereby yield high-quality acetic acid 19.

Please replace the paragraph beginning page 36, line 8 with the following amended paragraph:

The production rate of acetic acid (AC STY) was 19.4 mol/L·hr, the production rate of acetaldehyde (AD-STY) was 4.3 mmol/L·hr, and the ratio of the production rate of acetaldehyde to that of acetic acid (AD/AC) was 1/4500. The crude acetic acid 15 had a propionic acid (PA) content of 75 ppm by weight, a crotonaldehyde (CrD) content of 0.2 ppm by weight, and a residence time in the potassium permanganate test (~~chameleon-value~~ permanganate time) of 190 minutes.

Please replace the paragraph beginning page 36, line 24 with the following amended paragraph:

The above procedure was repeated, except for recycling the low-boiling component 10 via the line 12 to the reactor 3 without removing acetaldehyde therefrom. The resulting reaction mixture had an acetaldehyde content of 1050 ppm by weight, and the crude acetic acid had a propionic acid (PA) content of 180 ppm by weight, a crotonaldehyde (CrD) content of 1.6 ppm by weight, and a residence time in the potassium permanganate test (~~chameleon-value~~ permanganate time) of 40 minutes.

Please replace the paragraph beginning page 39, line 7 with the following amended paragraph:

The above procedure was repeated, except for recycling the low-boiling component 10 via the line 12 to the reactor 3 without removing acetaldehyde therefrom. The resulting reaction mixture had an acetaldehyde content of 820 ppm by weight, and the crude acetic acid had a propionic acid (PA) content of 120 ppm by weight, a crotonaldehyde (CrD) content of 0.5 ppm by weight, and a residence time in the potassium permanganate test (~~chameleon-value~~ permanganate time) of 160 minutes.

Please replace the paragraph beginning page 41, line 16 with the following amended paragraph:

The above procedure was repeated, except for recycling the low-boiling component 10 via the line 12 to the reactor 3 without removing acetaldehyde therefrom. The resulting reaction mixture had an acetaldehyde content of 710 ppm by weight, and the crude acetic acid had a propionic acid (PA) content of 115 ppm by weight, a crotonaldehyde (CrD) content of 1.4 ppm by weight, and a residence time in the potassium permanganate test (~~chameleon-value~~ permanganate time) of 80 minutes.

Please replace the paragraph beginning page 43, line 17 with the following amended paragraph:

The above procedure was repeated, except for recycling the low-boiling component 10 via the line 12 to the reactor 3 without removing acetaldehyde therefrom. The resulting reaction mixture had an acetaldehyde content of 800 ppm by weight, and the crude acetic acid had a propionic acid (PA) content of 600 ppm by weight, a crotonaldehyde (CrD) content of 3.0 ppm by weight, a hexyl iodide content of 100 ppb by weight, and a residence time in the potassium permanganate test (~~chameleon-value~~ permanganate time) of 30 minutes.

Please replace the paragraph beginning page 47, line 3 with the following amended paragraph:

When the low-boiling component is recycled to the reactor without removing acetaldehyde therefrom as shown in "Crude acetic acid a" in Table 2, Examples 1 to 3 show a

very small ratio of the production rate of acetaldehyde to that of acetic acid of 1/1500 or less, thereby significantly inhibit the by-production of consecutive reaction products of acetaldehyde, and show marked reduction in propionic acid content and crotonaldehyde content in the "crude acetic acid a" of about 1/2 to 1/10 those in Comparative Examples 1 and 2. According to Examples 1 to 3, 25 to 50 percent by mole of acetaldehyde is removed from the low-boiling components, and the remainder is recycled to the reactor to keep the acetaldehyde content of the reaction mixture to 500 ppm or less. Thus, the propionic acid content and the crotonaldehyde content in the "crude acetic acid b" are very low, the formation of byproducts derived from these compounds are inhibited, and the ~~ehameleon value~~ permanganate time is high as shown in "crude acetic acid b" in Table 2. In contrast, in Comparative Example 1, the ratio of the production rate of acetaldehyde to that of acetic acid is as great as 1/1200, and the "crude acetic acid b" has a high propionic acid content, a high crotonaldehyde content, and a low-~~ehameleon value~~ permanganate time, although the acetaldehyde removal percentage is 66 percent by mole, higher than those of Examples 1 to 3.